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APPLICATION OF LASERS IN SPECTROSCOPIC ANALYSIS

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ABSTRACT. The application of lasers to spectroscopic analysis to be used in metallurgical analysis, with reference to Raman spectroscopy and laser microprobes, is discussed.

1. Introduction

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At the present time, spectroscopic analysis can be divided up into three main fields: electron ray spectroscopy, magnetic wave spectroscopy (photo-spectroscopy), and ion spectroscopy. Almost the only one of these in which laser light is used is magnetic wave spectroscopy, that is, photospectroscopy. Laser light is applied only rarely in ion spectroscopy, that is, mass spectrometry. Concerning the principles of lasers, that is, population inversion, pumping, and oscillation, the reader is referred to the various explanations which have already been made public in considerable numbers [1 - 8]. This paper also will not touch upon plasma measurement by lasers [5, 6, 9, 10], which has been described in these explanations and reports, and concerning which an extremely large number of reports have been published recently.

Light from lasers (light amplification by stimulated emission radiation) has the following characteristics which differ from light coming from conventional light sources: (1) The monochromatic characteristics are extremely good; (2) The coherence is extremely good; (3) The directivity is extremely good. Spectroscopy makes up the groundwork for the basic principles of lasers,

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and various spectroscopic techniques are applied in observations and in research on laser substances. However, this paper deals with the application of lasers to spectroscopy, utilizing the three characteristics mentioned above; that is, particularly to the spectroscopic analysis of "solids". The applications of lasers to solids, chiefly metals and alloys, may be divided up into two categories: the utilization of laser light as light — that is, in Raman spectroscopy — and its utilization as heat. In the latter case, ruby or neodymium pulse lasers are condensed on the specimen, and are used as the source of evaporation heat to cause evaporation of matter. The chief application is for emission spectroscopic analysis. In the following, these two categories are explained simply.

2. Application as Light

The typical example of the application of laser light as light to spectroscopic analysis is Raman spectroscopy. The Raman spectra themselves have already been explained in numerous textbooks. At a very early period, Porto and Wood [11] applied ruby lasers as the light source for Raman spectra. Less than ten years later, convenient laser-Raman devices using gas lasers as the light source have already been placed on the market. The laser light sources used in these devices are argon ion (Ar^+) lasers, helium-neon (He-Ne) lasers, or krypton ion (Kr^+) lasers. Laser light with an output of 100 - 250 mW, and sometimes of 1 W, is used, at 4,800 Å or 5,145 Å for the Ar^+ lasers, 6,328 Å for the He-Ne lasers, and 6,471 Å for the Kr^+ lasers.

As was mentioned briefly in the preceding section, these lasers used as light sources have the following characteristic features:

(1) The spectral line width is sharp. (It is 0.005 nm for He-Ne lasers, and 0.025 nm for conventional mercury arc light sources.)

(2) It is possible to extract light with uniform spatial and temporal phases — that is, the light is coherent.

(3) It is possible to make up beams with a strong directivity.

(4) There is an extremely high intensity per unit area, per unit wave number.

(5) The output can be extracted as nearly perfect, linearly polarized light.

Therefore, it would appear that lasers would be disadvantageous for the measurement of Raman scattered light (the intensity of which is inversely proportional to the fourth power of the wavelength), because the wavelength is longer than in cases when spectral lines of 4,358 Å or 4,047 Å of conventional mercury arcs are used. However, this can be covered sufficiently by using high-output laser light. Furthermore, it has also become easy to measure substances with absorption in their visible section, or fluorescent materials. The inability to do this was one of the limitations on Raman spectroscopy in the past.

An example of a laser-Raman optical arrangement is shown in the diagram in Figure 1. All of these devices are almost exactly the same, except for a few slight differences in the method of setting up the samples, or in the method of eliminating naturally emitted rays. In addition to these technical problems, it has become possible to utilize the high efficiency of the incident light. It also is possible to solve the relative measurements of Raman polar-

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izability and of the tensor components, as well as the measurements of absolute intensity of Raman scattering, from the Raman scattering intensity.

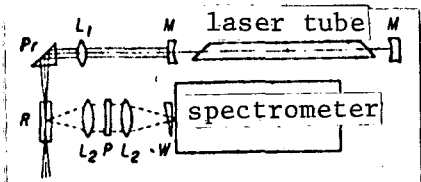


Figure 1. Laser-Raman optical arrangement.

By far, the most frequent field of application of laser-Raman spectroscopy is application to organic substances (liquids, solids, powders) [12 - 15]. This is true

because the Raman lines can almost always be observed with the naked eye, especially in the case of transparent liquids and solids. Furthermore, it has become possible to observe the Raman lines caused by weak overtones and combination tones, which it was nearly impossible to observe in the past. Let us introduce very simply examples of applications in spectroscopic analysis, mainly to alloys or solid inorganic compounds.

(1) Laser-Raman Measurements of Properties of Solids

Rather than being used for qualitative or quantitative analysis of inorganic substances, Raman spectroscopy has been used, although on a very limited scale, in estimating the structure of liquids or gaseous specimens [16 - 18]. On the other hand, in research on inorganic solid substances, the measurement of the electronic Raman effect is being viewed with interest from the standpoint of spectroscopic analysis. The electronic Raman effect is a Raman effect accompanied by transition between the normal state and the excited state of the localized center (impurities, lattice defects, etc.) contained within the substance. It differs from the lattice Raman effect, which results from lattice vibrations, and only the Stokes lines are observed.

Using He-Ne lasers as their light source, Koningstein et al. [19 - 21] investigated the excitation level of Eu^{3+} and Yb^{3+} in YGaG , as is shown in Table 1.

Since the intensity of the electronic Raman scattered light is determined by the number of localized centers contained in the solids it is, therefore, weaker than the lattice Raman scattered light. For this reason, there are various defects. For instance, the laser light must have a great output, and one must have equipment capable of performing measurements with a high efficiency. There must also be equipment for cooling the samples.

Electronic Raman scattering is also measured by means of acceptors of the neutral Zn and Mg contained in GaP [23]. In this case, measurements were

TABLE 1. ELECTRONIC RAMAN SCATTERED LIGHT OF R.E.
ELEMENTS IN YGaG [19]

Measuring system	Electronic Raman lines $\Delta\nu$ (cm^{-1})	Approximate assignment
Yb ³⁺ in YGaG	550	$O \rightarrow {}^2F_{1/2}$
Eu ³⁺ in YGaG	308 348 390	$O \rightarrow {}^7F_1$
Ed ³⁺ in YGaG	80	
Eu ³⁺ in Yt-Vanadate	359.5 404.5 970 995 1018 1067	$\dots O \rightarrow {}^7F_1$ $\dots O \rightarrow {}^7F_2$

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performed at 20° K, using two types of light: He-Ne laser light of 6,328 Å (50 mW) and of 6,118 Å (2 mW). The results are shown in Figure 2. The excited state of the acceptor corresponds to the following transitions. A: transition from the normal state, featured by quadruple contraction. Actually, separation occurs at intervals of 1 meV on account of microscopic stress on the periphery of the acceptor. In this transition, separation is magnified when external stress is applied to the crystals. B: transition from the normal state to the first excited state. C: transition from the normal state to the high-level excited state. D: transition to the valence electron band. In other words, in addition to the longitudinal optical (longitudinal mode optical phonon) (LO) and the transverse optical (transverse mode optical phonon) (TO), peaks corresponding to the above-mentioned transitions A, B, C, and D also are accompanied by an acoustic phonon. On account of external stress, A appears clearly separated about 6 meV away from the laser line, as is shown in Figures (a) and (b).

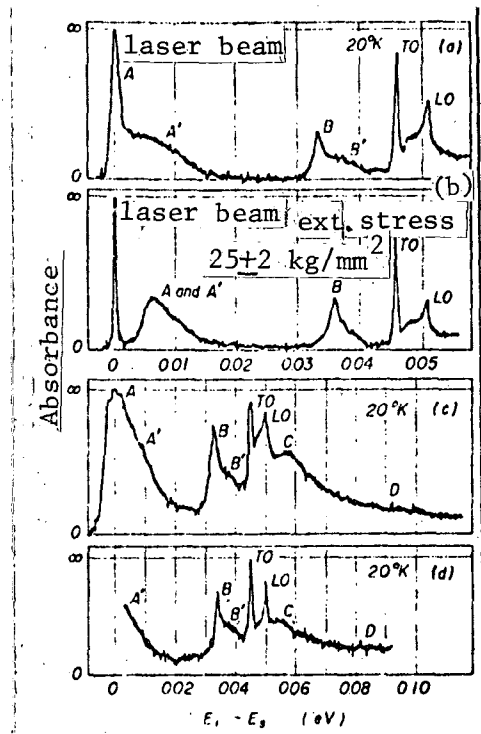


Figure 2. (a) low-energy section of Zn acceptor spectrum [23];
 (b) when external stress was applied to (a);
 (c) full spectrum of Zn interceptor;
 (d) full spectrum of Mg acceptor.

Figures (c) and (d) are a comparison of the Zn acceptor and the Mg acceptor. The peaks due to the lattice Raman scattering have the same energy in both cases, but the peaks corresponding to the B and C transitions have a difference of one or more meV. As for the electronic Raman of the P donor in Si and the B acceptor, measurements were performed at the He temperature, using Nd^{3+} YAG lasers of 1.0648μ as the light source [22]. The results, as shown in Figure 3, were 13.1 meV in the P donor, and 23.4 meV in the B acceptor.

As is clear from the foregoing, the electronic Raman effect can be a very useful tool in carrying out some of the research in localized centers such as impurities or lattice defects. Laser-Raman spectroscopy is also applied in another way to the properties of solids. That is, it is applied to research on ferroelectric substances. Most of this is research concerning the soft mode of ferroelectricity.

There are numerous monographs about BaTiO_3 , KTaO_3 , etc. [24 - 28]. In addition, laser-Raman spectroscopy is being actively applied to research on Raman scattering caused by solid plasma and to research on the properties of semiconductors such as InSb, GaAs, and ZnTe, such as the nonparabolicity of the energy bands [29 - 33].

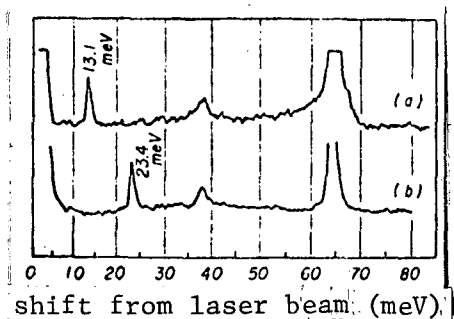


Figure 3. Raman spectra of impurities in Si at 4.2° K [22].

As for the lattice Raman effect for metal alloys which are not semi-conductors, measurements have been made for Be and AuAl₂ [34]. Raman lines appear at 300° C when using Ar⁺ lasers at 455 cm⁻¹ for Be, and at 266 cm⁻¹ for AuAl₂. The Raman intensity of Be is about one-tenth that of Ge [35], and this difference is said to be connected to changes in the electronic polarizability of the metal caused by lattice deformation.

However, there is intense interest in the fact that the application of laser-Raman spectroscopy makes it possible to measure the lattice Raman effect of metals, although the Raman spectra of these metals reveal a high background because of the scattered light from the metal surface.

3. Application as Heat

Lasers have been utilized for quite a long time as heat sources (sources of material evaporation) in spectroscopic analysis, particularly emission spectroscopic analysis. CO₂ gas lasers are almost never used in this. In most cases, a laser microprobe method is used, in which ruby laser beams or Nd laser beams are condensed by lenses on the substance, causing localized material evaporation, and this part is subjected to spectroscopic analysis. The methods of spectroscopic analysis used are emission spectroscopy, atomic absorption spectrophotometry, and mass spectrometry.

(1) Material Evaporation

Concerning utilization of laser beams as heat sources, a comprehensive report from the welding standpoint has already been published in this journal [36]. Two or three monographs dealing with material evaporation by lasers

from the standpoint of spectroscopic analysis have already been reported [37 - 39]. Concerning the evaporation behavior of matter — that is, concerning the amount of evaporation of matter and the relationship between the evaporation phenomenon and laser energy — there is a monograph by Strasheim et al. [39], which also includes a report on spectroscopic chemistry. Klocke [37] demonstrates that the size and depth of the crater formed when laser light is condensed on a metal surface vary, depending upon the type of the metal and the laser energy (0.5 - 1.5 Ws), as is shown in Figure 4 and Photographs 1, 2, and 3. Ready [40] has calculated the depth of the crater from Landau's model concerning evaporation [41], and has compared this with the actual value. The results are shown in Table 2. As for the discrepancies between the calculated and experimental values for Sn, Bi, Pb, Cd, and Mg, they are attributed to differences in the thermal conductivity, the vapor pressure, and the reflection energy, but nothing is said about them in detail. However, it is demonstrated that in the case of Bi, Pb, Sn, and Ag there is a linear relationship between the quantity at which evaporation ceases to take place and the energy of the lasers. The relationship is that shown in Figure 5.

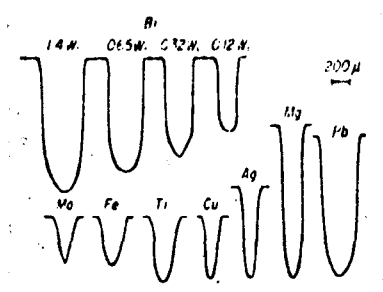


Figure 4. Crater cross section
(lower row: laser energy 1.4 Ws.)
[37].

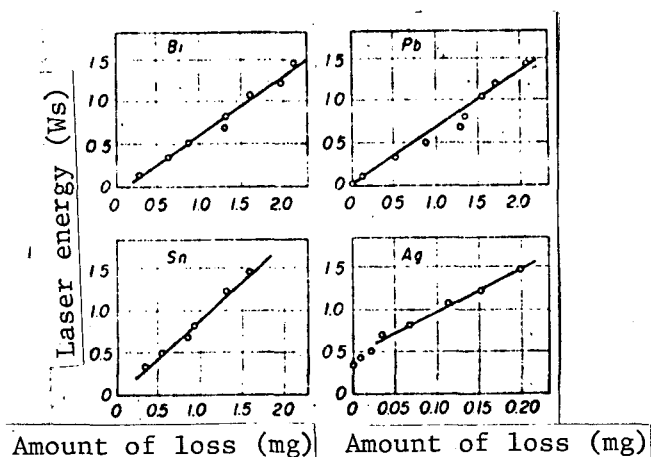
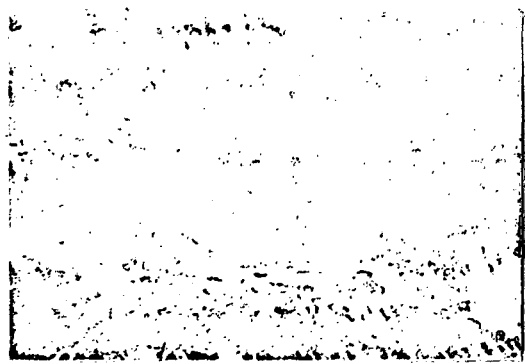


Figure 5. Relationship between laser energy and amount of evaporation loss [37].

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Photograph 1. Vicinity of crater on copper surface [37]. (30 X 2/3)



Photograph 2. Crater in copper [37]. (150 X 2/3)



Photograph 3. Crater in lead [37]. (50 X 2/3).

As for emission spectroscopic measurements, studies have been made of the temporal changes in the bright line spectrum and the continuous light of Al when Al alloys were irradiated with laser beams [39], and high-speed camera observations have also been made of the evaporation phenomena of samples using a laser microprobe rather than time-divided photometry [42]. This has provided interesting results concerning material evaporation by lasers.

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(2) Emission Spectroscopic Analysis by Lasers

As was mentioned above in (1), at around the same time as research was performed on material evaporation by means of laser microprobes, attempts were also made to apply laser microprobes to emission spectroscopic analysis. A

TABLE 2. DEPTHS OF CRATERS MEASURED
BY LASERS (COMPARISON OF ACTUAL MEASURED VALUES
WITH CALCULATED VALUES OBTAINED USING LANDAU'S
MODEL) [37]

Elements	Measured values (μm)	Calculated values (μm) (reflection energy corrected)
Sn	1586	2100
Bi	1516	4700
Cd	1648	4240
Pb	1554	3810
Mg	1676	3150
Ag	960	925
Cu	830	615
Ti	753	—
Ni	660	—
Fe	538	675
Mo	570	550

considerable number of different types of devices for laser micro-emission spectroscopic analysis have already been put onto the market, in the same way as devices for laser-Raman spectroscopy. Basically, these devices condense laser light from neodymium glass or a ruby on the surface of a specimen under an optical microscope, so as to subject the substance to photo-excitation by the condensed

laser light. Or in some cases, spectroscopy of the light is performed when re-excitation is performed by introducing arc or spark discharges in the plasma produced by material evaporation.

The different devices are basically assembled in the sequence shown in Figure 6 [43], the only differences between them being that there are slight differences in the optical system in each device. Katsuno et al. [44] have provided an explanation of these points. There are also many general studies concerning laser microprobe emission spectroscopy, relating to the analysis of metals, ores, biological organisms, and archeological specimens [45]. There are also the following problems:

In terms of the technical aspects of spectroscopic analysis, there are little differences from ordinary spectroscopic analysis. However, when the laser light is condensed to about $50 \sim 100 \mu\phi$ to perform localized analysis

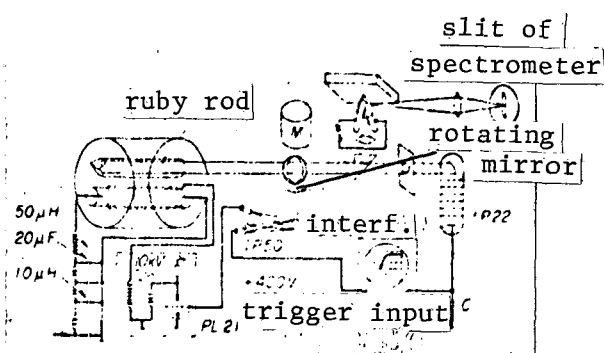


Figure 6. Laser arrangement for spectroscopic analysis [43].

of a substance, it is difficult to prepare standard substances with a homogeneity on the micron order. In view of the fact that localized analysis of microscopic sections is performed, one cannot use the internal standard method or the standard addition method which are used in ordinary spectroscopic analysis. Of course, this does not apply to cases when this laser probe is applied in the analysis of extremely small amounts of specimens. Furthermore, the effects of the atmosphere are clearly observable, exactly as in ordinary emission spectroscopic analysis [46, 47].

One also ought to consider the possibility that the atmospheric gases themselves may be excited by lasers. Especially in cases when specimens have been excited by an immense pulse, the evaporated matter does not play an effective role in photoexcitation, and one observes self-reversal or expansion of the spectral line width because of pressure effects due to the presence of many atoms and molecular substances (in a certain sense, the presence of a thick plasma) [48]. The introduction of arcs and sparks by auxiliary electrodes is performed also for the purpose of preventing this. It is recommended that the reader consult the reports concerning different specimens and various analytical methods. Here let us consider only a few examples of special types of analysis using this laser probe. /154

Two types of discharge phenomena are observed in argon streams: condensed discharge and diffuse discharge. Lasers are used as initiators to obtain condensed discharge [47]. Runge et al. [49] performed emission analysis of metals in the molten state, utilizing the characteristics of laser beams. Felske [50] has attempted plane analysis, although not continuously, with a 0.1 Ws Q

switch and a ruby laser, moving the specimen forwards and backwards, and right and left at definite intervals. In addition to these, another interesting research method is to combine this localized analysis with micro-infrared ray absorption spectra [51]. The techniques of localized analysis which are available at the present time are the electron probe microanalyzer (EPMA) and the ion microprobe mass analyzer (IMMA) [52, 53]. Table 3 gives comparative data on the advantages and disadvantages of these, as compared with the laser microprobe (LMP).

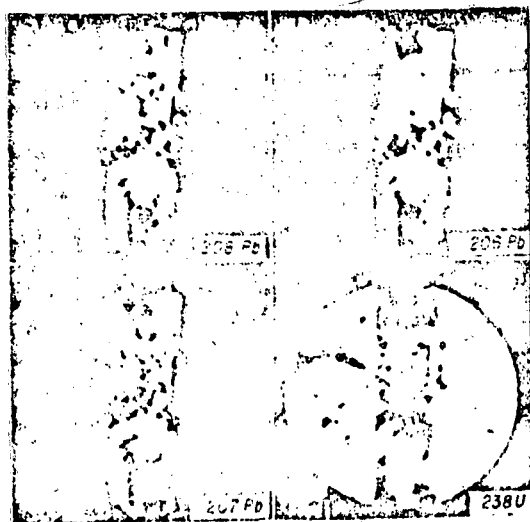
(3) Atomic Absorption Analysis Applying a Laser Light Source

The following attempt was made to apply lasers in atomic absorption analysis. Laser beams (ruby or neodymium) were condensed on the surface of the specimen to be analyzed to induce material evaporation. At the same time, light from the primary light source (a xenon lamp) was passed through the material cloud which had assumed an atomized state. The amount of absorption was measured in order to analyze the elements in the substance. There is a report of Mossotti et al. [54] on this attempt. As was already mentioned in (2), when the spectrum pattern of material excitation by laser beams themselves is observed, the presence of atomic elements can be readily assumed from the expansion of the line width and from the appearance of self-absorption. Oscilloscope measurements are performed, although this is not an accurate quantitative analysis. An example of this is shown in Photograph 5. In this case, the type of the matrix affects the detection sensitivity, in the same way as in emission spectroscopy. The effects of this are shown in Figure 7. Thus, there are very few examples of applying laser beams to atomic absorption analysis, but the method is an interesting one in that it does not use aqueous solution specimens.

(4) Mass Spectroscopy Using Laser Beams

The application of laser beams to mass spectroscopy is exactly the same as the application of laser probes to emission spectroscopic analysis. It is

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Photograph 4. Isotope distribution of lead in pitchblende [53].

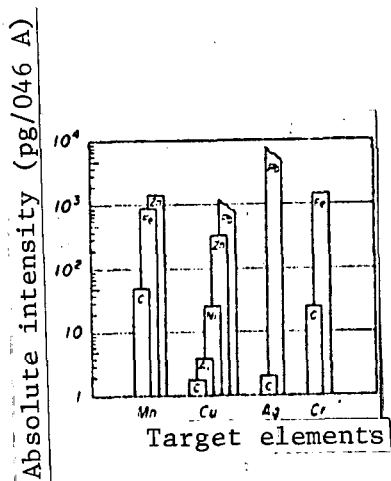
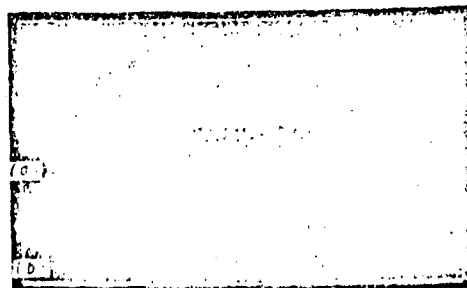


Figure 7. Influence of matrix on absolute intensity. The columns represent the matrixes. The point where a column is interrupted in a wavy pattern indicates the level at which it became impossible to detect the given element [54].



Photograph 5. Example of observation of the absorption of 1% Mn (4031 Å) in Zn by an oscilloscope [54].

- (a) Signal from primary light source and background;
- (b) Signal after passing through laser cloud.

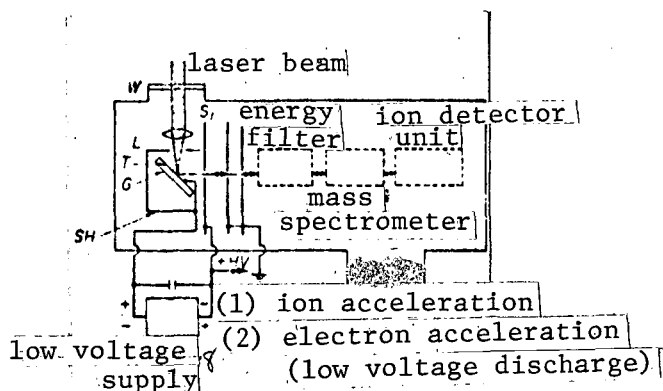


Figure 8. Schematic diagram of ion source unit in a solid mass spectrograph.

TABLE 3. COMPARISON OF TYPICAL METHODS OF LOCALIZED ANALYSIS

Method	LMP	EPMA	IMMA
Excitation source	Light (electromagnetic waves)	Electron rays	Ion beams (Ar, O ₂ , N ₂ , Cl ₂ , etc.)
Condensing method	Optical lens	Condenser lens	Condenser lens
State of excitation	Considerable material evaporation	Almost no material evaporation	No material evaporation (spattering)
Size of analyzed part	~20μφ	~0.5μφ	~2μφ
Depth of analyzed part	10 ~ 200μ	~0.5μ	Variable in vertical direction to Å order
State of analyzed part	No strict limitations. No need for electrical conductivity.	Smoothness necessary. Electrical conductivity.	Smoothness not very necessary. Electrical conductivity not necessary.
Specimen chamber	Vacuum not needed except for special purposes.	Vacuum necessary	Vacuum necessary
Equipment	Large-size equipment not necessary	Quite large size	Quite large size
Elements which can be analyzed	Li(3) (in some cases H(1) ~)	Be(4) ~	H(1) ~
Analysis	In photographic measurement, almost all elements can be photographed. Continuous, linear, plane analysis is impossible.	Observation and measurement of element distribution images possible. Micro-diffraction (measurement of Kossel's lines) possible.	All elements photographed on grid plate. Observation of element distribution images (isotope distribution images, Photograph 4) possible.

considered in terms of the arrangement shown in Figure 8 [55 - 57]. There are two possible methods. In the first, the evaporation material does not pass through another special ionization process, but is admitted into the ion acceleration section. In the other, in the same way as when emission spectroscopy is performed in the material evaporation section, arcs or sparks are introduced to perform ionization, and the specimen is introduced into the ion acceleration section. In the former case, the distribution of the ion energy is narrow, and in the distribution of valence electrons there is a large number of M^+ . In the second method, various types of valence electrons — such as M^+ , M^{2+} , and even M^{3+} — are produced. Consequently, a mass spectrometer with a high resolving power is necessary.

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An actual problem presented in spectroscopic analysis by means of solid lasers is the service life of the laser rod. (The laser rod's service life is said to terminate after about 10,000 emissions.) At the present time, the laser rod cannot be said to be an entirely practical excitation source for spectroscopy in every way.

In the foregoing, the applications of lasers to spectroscopic analysis which were felt to be of interest to persons engaged in metallurgical analysis were discussed with reference to Raman spectroscopy and laser microprobes. It is feared that significant research may possibly have been omitted. The writer will be pleased if readers will favor him with their comments and suggestions.

REFERENCES

1. Birnbaum, G. Optical Masers, Advances in Electronics and Electron Physics. Suppl. 2, Academic Press, 1964.
2. Heavens, O. S. Optical Masers. Methuen, 1964.
3. Lengul, L. A. Laser. John Wiley and Sons, 1963.
4. Okada, Arata. Purazuma kogaku (Plasma Engineering). Nikkan Kogyo Shimbun, 1970, p. 659.
5. Tanaka, Yokoyama. Purazuma to sono oyo sochi (Plasma and Devices for its Application). Nikkan Kogyo Shimbun, 1971, p. 165.
6. Shimazu. Bunko kenkyu. Vol. 19, 1970, p. 268.
7. Misu. Bunko kenkyu. Vol. 11, 1963, p. 57.
8. Namba, Kin. Oyo butsuri. Vol. 32, 1963, p. 442.
9. Yamanaka. Oyo butsuri. Vol. 34, 1965, p. 628.
10. Damon, E. K. et al. Appl. Optics, Vol. 2, 1963, p. 546.
11. Porto, S. P. S. and D. L. Wood. J. Opt. Soc. Amer., Vol. 52, 1962, p. 521.
12. Hendra, P. J. and C. J. Vear. Analyst, Vol. 95, 1970, p. 321.
13. Brandmuller, J. Natur Wiss., Vol. 21, 1967, p. 293.
14. Hendra, P. J. and E. J. Loader. Nature, Vol. 217, 1968, p. 637.
15. —. Nature, Vol. 216, 1967, p. 789.
16. Hayward, G. C. and P. J. Hendra. Spectrochim. Acta, Vol. 23 A, 1967 p. 2309.
17. Hendra, P. J. and Z. Jovie. J. Chem. Soc., Vol. (A), 1968, p. 600.
18. Hendra, P. J. and M. M. Qurashi. J. Chem. Soc., Vol. (A), 1968, p. 2963.
19. Koningstein, J. A. J. Chem. Phys., Vol. 46, 1967, p. 2811.

20. Koningstein, J. A. and O. S. Martensan. Phys. Rev. Letters, Vol. 18, 1967, p. 83.
21. Koningstein, J. A. J. Opt. Soc. Amer., Vol. 57, 1966, p. 1405.
22. Wright, G. B. and A. Mooradian. Phys. Rev. Letters, Vol. 18, 1967, p. 608.
23. Henry, C. H. et al. Phys. Rev. Letters, Vol. 17, 1966, p. 1178.
24. Fleury, P. A. and J. M. Warlock. Phys. Rev. Letters, Vol. 18, 1967, p. 665.
25. Pinczuk, A., W. Talor and K. Burstein. Solid State Comm., Vol. 5, 1967, p. 429.
26. DiDomenico, M, Jr., S. P. S. Port and S. H. Wemple. Phys. Rev. Letters, Vol. 19, 1967, p. 855.
27. Nilsen, W. G. and J. G. Skinner. J. Chem. Phys., Vol. 47, 1967, p. 1413.
28. Rimai, L., J. L. Parsen and J. T. Hickmott. Phys. Rev., Vol. 168, 1968, p. 623.
29. Mooradian, A. and G. B. Wright. Phys. Rev. Letters, Vol. 16, 1966, p. 999.
30. Slusher, R. E., C. K. N. Patel and P. A. Fleury. Phys. Rev. Letters, Vol. 18, 1967, p. 77.
31. Patel, C. K. N. and R. E. Slusher. Phys. Rev., Vol. 167, 1968, p. 413.
32. Patel, C. K. N., R. E. Slusher and P. A. Fleury. Phys. Rev. Letters, Vol. 17, 1966, p. 1011.
33. Irwin, J. C. and J. La Come. J. Appl. Phys., Vol. 41, 1970, p. 1444.
34. Feldman, D. W., J. H. Parker and M. Ashkin. Phys. Rev. Letters, Vol. 21, 1968, p. 607.
35. Parker, H., D. W. Feldman and M. Ashkin. Phys. Rev., Vol. 155, 1967, p. 712.
36. Arata. Kinzoku Gakkai kaiho, Vol. 8, 1969, p. 243.
37. Klocke, H. Spectrochim. Acta, Vol. 24 B, 1969, p. 263.
38. Bogerhausen, W. and R. Vesper. Spectrochim. Acta, Vol. 24 B, 1969, p. 103.

39. Scott, R. H. and A. Strasheim. *Spectrochim. Acta.*, Vol. 25 B, 1970, p. 311.
40. Ready, J. F. *J. Appl. Phys.*, Vol. 36, 1965, p. 462.
41. Landau, H. G. *Quart. Appl. Math.*, Vol. 8, 1950, p. 81.
42. Nakajima, Yoshida, et al. Materials for the Summer Seminar of the Japan Spectroscopy Association. Light Source Study Group.
43. Hagenah, W. D. *ZAMP*, Vol. 16, 1965, p. 130.
44. Katsuno, Takeuchi, Sunahara, Morita. *Bunseki kagaku*, Vol. 17, 1968, p. 376.
45. For example, Yamane, Suzuki, Matsumoto. *Bunko kenkyu*, Vol. 19, 1970, p. 147.
46. Suzuki, Ando. Third Tokyo Discussion Meeting on Applied Spectrometry.
47. Hagenah, W. D., K. Hirokawa and K. Laqua. *XII Colloquium Spectroscopicum International Exter*, 1965, p. 333.
48. Karyakin, A. U., M. U. Akhwanova and V. A. Kaigordov. *Zhr. Aval. Khim.*, Vol. 20, 1965, p. 145.
49. Runge, E. F., R. W. Minck and F. R. Brym. *Spectrochim. Acta*, Vol. 22, 1966, p. 1678.
50. Felske, A., H. D. Hagenah and K. Laqua. *Z. Anal. Chem.*, Vol. 216, 1966, p. 50.
51. Moenka, H., L. Moenke et al. *Kristall und Technik*, Vol. 1, 1966, p. 351.
52. Liebl, H. *J. Appl. Phys.*, Vol. 38, 1967, p. 5277 and elsewhere.
53. Rouberal, J. M., et al. *Vth International Congress on X-ray Optics and Microanalysis*, Springer-Verlg., 1968, p. 311.
54. Mossotti, V. G., K. Laqua and W. D. Hagenah. *Spectrochim. Acta.*, Vol. 23 B, 1967, p. 197.
55. Honig, R. E. and J. R. Woolston. *Appl. Phys. Letters*, Vol. 2, 1963, p. 138.
56. Honig, R. E. *Appl. Phys. Letters*, Vol. 3, 1963, p. 8.
57. Ban, V. S. and B. E. Knox. *J. Chem. Phys.*, Vol. 52, 1970, p. 243.

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